Light-Induced Excited States in H$^-$

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We present a nonperturbative, fully correlated calculation of the structure of H$^-$ in an intense laser field, based on the high-frequency Floquet theory. We show that, as the intensity increases at sufficiently high frequencies, the electron affinity manifests a peculiar behavior and can become substantially higher than its field-free value. Besides, H$^-$ acquires excited states, some of which are doubly excited and nonautodetaching. At high intensities H$^-$ undergoes stabilization, similarly to the H atom.

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The behavior of several-electron atoms in intense laser fields, when electron correlation and nonperturbative field effects are comparable in magnitude, is a formidable problem in its incipient stages of solution [1]. In the field-free case, H$^-$ has been used as a test case for the ability of quantum mechanical methods to describe electron correlation because, besides its simplicity, it involves correlation to the highest degree [2]. Indeed, as H$^-$ has only one bound state in the manifold ^1S_g ($L=0$, $S=0$, even parity) [3], with the small electron affinity $J=0.0227$ a.u.$=0.751$ eV, a highly correlated eigenfunction is needed to describe it.

We now study the behavior of H$^-$ in intense fields as a test case for the competition between electron correlation and nonperturbative field effects. We apply the high-frequency theory of laser-atom interactions [4] with full electron correlation included. For hydrogen in a linearly polarized field and at large values of the parameters ω and $\alpha_0=I^{1/2}\omega^{-2}$, where ω and I are the frequency and intensity [5], the theory has revealed the existence of oscillating dichotomous electron states [4,6]. The generalization of the theory to two-electron atoms has led Mittleman [7] to conclude that H$^-$ also has a dichotomy (large-α_0) limit, its total energy being twice that of H under the same conditions. It was then shown by Gavrila and Shertzer [8] that in this limit H$^-$ exhibits excited states, some of them corresponding to two-electron excitations. These results do not indicate, however, how this limiting situation is reached, or how the electron correlation varies in the process. As opposed to Refs. [7] and [8], we are interested here in moderate values of α_0 ($\alpha_0<45$). No results have been published yet on the multiphoton ionization of H$^-$ in the superintense regime.

To carry out our study we start from the space-translated form of the Schrödinger equation for a two-electron atom in a linearly polarized field of vector potential $\mathbf{A}=-a\mathbf{e}\sin\omega t$ [4,9]:

$$\{-\tfrac{1}{2}(\Delta_1+\Delta_2)+V(\mathbf{r}_1+\boldsymbol{\alpha}(t))+V(\mathbf{r}_2+\boldsymbol{\alpha}(t))+1/r_{12}\}\Psi = i\frac{\partial\Psi}{\partial t}, \quad (1)$$

where $V=-1/r$ and $\boldsymbol{\alpha}(t)=\alpha_0\mathbf{e}\cos\omega t$ [5]. By extending the stationary approach used in the one-electron case [4] it can be shown [8] that Eq. (1) is equivalent to a system of coupled equations for the Floquet components of Ψ. At sufficiently high frequencies ω this system reduces approximately to the following equation for the structure of the two-electron atom:

$$\{-\tfrac{1}{2}(\Delta_1+\Delta_2)+V_0(\mathbf{r}_1,\alpha_0)+V_0(\mathbf{r}_2,\alpha_0)+1/r_{12}\}\Phi = W\Phi. \quad (2)$$

Here, V_0 is the "dressed" Coulomb potential, which can be viewed as the potential generated by smearing out the proton charge on the line extending between $\pm\alpha_0\mathbf{e}$, with a higher concentration near the end points (see [4,6]). Equation (2) has obviously real eigenvalues $W(\alpha_0)$ that do not depend explicitly on ω. For the n-photon ionization amplitudes one finds

$$f_{n\gamma}(\hat{\mathbf{f}}) = -(1/\pi)\langle\Phi^{(-)}_{\gamma,\mathbf{k}_{n\gamma}}|V_n|\Phi_0\rangle, \quad (3)$$

where V_n is a transition operator. Both the initial and final state wave functions Φ_0 and $\Phi^{(-)}_{\gamma,\mathbf{k}_{n\gamma}}$ are symmetrized solutions of Eq. (2), the former being a bound state solution, the latter a continuum solution corresponding to an ejected electron of momentum $\mathbf{k}_n$ and a residual atom in state γ.

We are primarily interested here in the structure of H$^-$ in intense fields. Because of the axial symmetry of V_0, the eigenfunctions of Eq. (2) can be grouped into manifolds characterized by Λ, the absolute value of the total magnetic quantum number with respect to the field axis, by the parity P (g or u), and by the total spin S; hence the notation $^{2S+1}\Lambda_P$ for the manifolds, and $^{2S+1}W^P_{\Lambda j}(\alpha_0)$ for the energies they contain, with j a labeling index. This is quite similar to the way H$_2$ is described in the absence of a field.

The calculation of the eigenvalues of Eq. (2) was carried out in prolate spheroidal coordinates ξ,η,ϕ [10], centered on the end points $\pm\alpha_0\mathbf{e}$. A two-electron basis set was introduced in the form of (appropriately symmetrized) products of one-electron basis functions such as

$$(\xi-1)^p\eta^q[(1-\eta^2)(\xi^2-1)]^{m/2}e^{im\phi}e^{-\gamma\xi},$$

where p,q,m are positive integers. The resulting energy

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matrix was diagonalized, and convergence obtained by including up to 100 basis functions [11]. We estimate that our eigenvalues $W(\alpha_0)$ are calculated with a relative accuracy of better than 5×10^{-4}, and the electron affinity (see below) to better than 1%.

We present our numerical results for the detachment energies of H^- in Fig. 1. We define the detachment energy of a state by ${}^{2S+1}D^{P}_{\Lambda j}(\alpha_0)=E(\alpha_0)-{}^{2S+1}W^{P}_{\Lambda j}(\alpha_0)$, where $E(\alpha_0)$ is the ground state energy of H in the field. For the ground state the detachment energy coincides with the field dependent electron affinity, $J(\alpha_0)$. We recall that $|E(\alpha_0)|$ is a rapidly decreasing function of α_0; see Tables I of Refs. [6(a)] and [6(b)]. With the exception of one state, represented by curve b, we show in Fig. 1 only states (A-E) that belong to the ${}^1\Sigma_g$ manifold. The behavior of the ground state $A\,{}^1\Sigma_g$, the only one to exist for small α_0, is rather peculiar. As α_0 increases from 0, the electron affinity decreases from its field-free value of 0.75 eV to a minimum value of 0.6 eV, around $\alpha_0=2.5$. As α_0 increases further, the affinity increases to an absolute maximum of 1.1 eV, around $\alpha_0=17$, and thereafter decreases slowly. At $\alpha_0=45$, the largest value we have considered, $J(\alpha_0)=0.817$ eV, is still larger than the field-free value, whereas $|E(\alpha_0)|$ has reduced to 0.044 a.u.=1.2 eV. This clearly illustrates how drastically the nonperturbative field effects occurring at $\alpha_0>1$ can modify the electron correlation. The importance of the latter decreases as α_0 increases further and the problem reduces to one with two independent electrons.

Remarkable, however, is the *appearance of light-induced excited states* (states B-E of Fig. 1). After becoming bound at some value of α_0, their detachment energy increases to a maximum, and then decreases afterwards. Note that the first light-induced excited state to appear, for α_0 just above 3.50, belongs to the ${}^3\Sigma_u$ manifold; see curve b. (For $\alpha_0=3.55$ its detachment energy is at least 10 meV.) Curve b merges with curve A (just above $\alpha_0=10$) because of single-triplet coalescence [12].

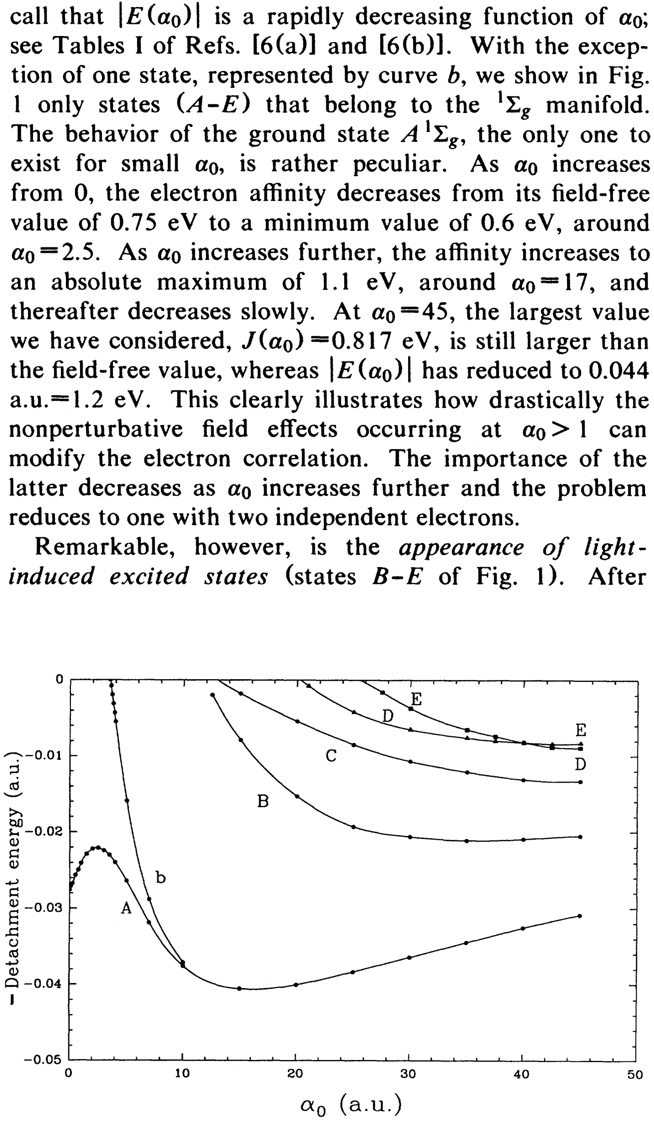

FIG. 1. Negative of the detachment energies of the ground state (A), and the lowest-lying light-induced states (B-E) of the ${}^1\Sigma_g$ manifold of H^- as a function of $\alpha_0=I^{1/2}\omega^{-2}$, where I is the intensity and ω the frequency. (All quantities are in a.u.) The lowest state of the ${}^3\Sigma_u$ manifold, $b\,{}^3\Sigma_u$, is also represented. Note the avoided crossing of the D and E curves around $\alpha_0=39$. E is a doubly excited state for $\alpha_0<39$, and this configuration is transferred to D for $\alpha_0>39$.

We would like to point out that light-induced excited states have been signaled before in one-dimensional short range potential models by Bhatt, Piraux, and Burnett, by Bardsley, Szöke, and Comella, and by Yao and Chu [13,14], and for hydrogen by Dörr, Potvliege, Proulx, and Shakeshaft [15]. In the present two-electron case their appearance is due to a different mechanism, namely, the interplay of nonperturbative field effects and electron correlation.

By comparing the shape and the nodal structure of the eigenfunctions of Eq. (2) with approximate wave functions we have obtained from an independent-electron calculation, it was possible to assign configurations to each of the states in Fig. 1 [16]. At $\alpha_0\approx30$ the resemblance of the wave functions was so good as to leave no doubt about the assignment. In this way $(B,C)\,{}^1\Sigma_g$ and $b\,{}^3\Sigma_u$ could be identified as singly excited states. For $\alpha_0<39$ the state $D\,{}^1\Sigma_g$ is a singly excited state, too, whereas $E\,{}^1\Sigma_g$ is a *doubly excited state* [12]. This is a *nonautodetaching* doubly excited state, subject to multiphoton ionization only, just like the other states [11]. However, curves D and E collide in the α_0 interval 39.0 ± 0.5. Although symmetry considerations require that the crossing should be avoided, the two curves come so close together that we could not tell them apart at $\alpha_0=39$ within the accuracy of our calculation. We have checked that the shape of the eigenfunctions for the two states is transferred diabatically at the crossing, from one curve to the other; i.e., the doubly excited configuration is transferred to the state $D\,{}^1\Sigma_g$ and the singly excited one to the state $E\,{}^1\Sigma_g$.

In Fig. 2 we illustrate the molecular character of the eigenstates $\Phi_0(\mathbf{r}_1,\mathbf{r}_2)$, and the electron correlation arising from it. We consider specifically the light-induced excited state $C\,{}^1\Sigma_g$ at $\alpha_0=30$, and represent the (unnormalized) two-electron probability density $|\Phi_0(\mathbf{r}_1,\mathbf{r}_2)|^2$ as a function of $\mathbf{r}_2$, when $\mathbf{r}_1$ is fixed at various points $\mathbf{r}_1=-\lambda\alpha_0\mathbf{e}$ $(0<\lambda<1)$, situated on the line of charges. Since, under the circumstances, $|\Phi_0|^2$ is axially symmetric with respect to $\mathbf{r}_2$ around the line of charge taken as the z axis, it is sufficient to represent it in an arbitrary plane passing through this axis. As apparent the probability density has sizable values over a linear extension along the z axis of about $2\alpha_0=60$; i.e., the atom can become extremely spread out. When $\mathbf{r}_1$ moves in from the end point $-\alpha_0\mathbf{e}$ $(\lambda=1)$ towards the origin $(\lambda=0)$, there is a drastic change in the shape of $|\Phi_0|^2$, as it tends to be pushed away from the vicinity of $\mathbf{r}_1$ by the electron-electron repulsion.

The wave functions $\Psi(\mathbf{r}_1,\mathbf{r}_2)$ and $\Phi_0(\mathbf{r}_1,\mathbf{r}_2)$ considered are solutions of Eqs. (1) and (2), respectively. To leading

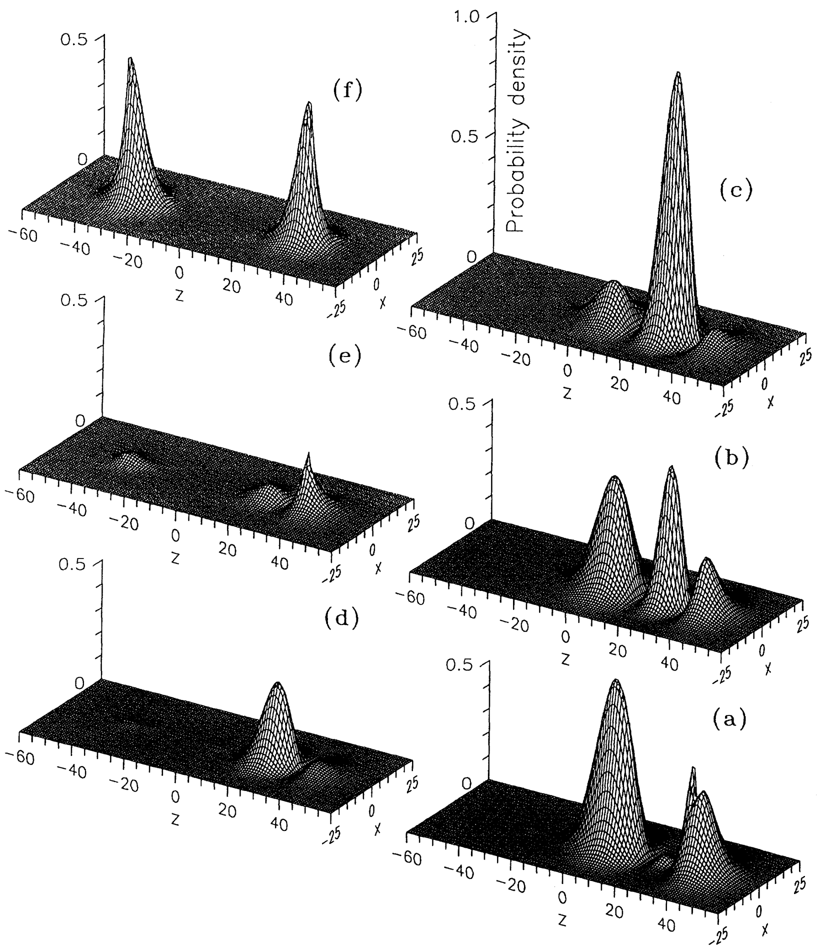

FIG. 2. Unnormalized probability density $|\Phi_0(\mathbf{r}_1,\mathbf{r}_2)|^2$ at $\alpha_0=30$ for the state $C\,^1\Sigma_g$ as a function of $\mathbf{r}_2$, when $\mathbf{r}_1$ is fixed at various points $\mathbf{r}_1(0,0,-\lambda\alpha_0)$ on the z axis taken along the "line of charge." Because of the axial symmetry, it is sufficient to represent $|\Phi_0(\mathbf{r}_1,\mathbf{r}_2)|^2$ in a plane passing through this axis. The plots correspond to (a) $\lambda=1$, (b) $\lambda=0.875$, (c) $\lambda=0.75$, (d) $\lambda=0.50$, (e) $\lambda=0.375$, and (f) $\lambda=0$. The normalized probability density is obtained by multiplication with 3.475×10^{-11}. All quantities are in a.u.

order $\Psi\cong\Phi_0\exp(-iWt)$. The wave function for the laboratory reference frame (in the momentum gauge) is given by

$$\psi_L(\mathbf{r}_1,\mathbf{r}_2,t)=\Psi(\mathbf{r}_1-\boldsymbol{\alpha}(t),\mathbf{r}_2-\boldsymbol{\alpha}(t),t)$$
$$\cong\Phi_0(\mathbf{r}_1-\boldsymbol{\alpha}(t),\mathbf{r}_2-\boldsymbol{\alpha}(t))\exp(-iWt)\,;$$

see Ref. [4]. It oscillates harmonically with amplitude α_0, and so do the probability densities derived from it.

We briefly address the question of the stability of H$^-$ under the circumstances described above. At low intensities the (dominant) $n=1$ amplitude given by Eq. (3) coincides with the known, many times calculated expression of the photodetachment amplitude; e.g., see [17]. At high intensities, in the dichotomy regime, the n-photon ionization rates of H$^-$, $\Gamma_n^{(-)}$, derived from Eq. (3), become the double of those of H under the same conditions, Γ_n: $\Gamma_n^{(-)}\cong2\Gamma_n$. This shows that the lifetime of H$^-$ is half that of H [8]. Consequently, just like H, H$^-$ too undergoes the phenomenon of (adiabatic) "stabilization," by which when increasing the intensity the lifetime *increases* (for H, see Refs. [4,14,18-20]). On the whole, H$^-$ appears to be about as stable as H at the same intensity and (sufficiently high) frequency. Stabilization has been shown to occur also in one-dimensional models of H$^-$, although not under the circumstances described here (see Ref. [1(h)], p. 1607, and Ref. [8] of that paper).

We conclude by noting that the behavior of the ground state of H$^-$ (level shift, ionization pattern) should be amenable to experimental verification [21]. The detection of the light-induced excited states, on the other hand, is likely to be quite challenging, although various procedures can be imagined [22].

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[4] A detailed discussion of the high-frequency Floquet theory for one-electron systems was given by one of us (M.G.) in the volume *Atoms in Intense Laser Fields*, edited by M. Gavrila (Academic, New York, 1992), p. 435.

[5] Atomic units are used throughout, except when otherwise noted. We take as atomic unit of intensity 3.51×10^{16} W/cm^2.

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[11] A detailed account will be given elsewhere.

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